



# Adsorption of Chromium (VI) from aqueous solution by using Bioactive Material *Macrotyloma uniflorum* seed powder

N. Gandhi<sup>1,2</sup> and D. Sirisha<sup>1</sup>

<sup>1</sup>Centre for Environment and Climate change, School of Environmental Sciences, Jawaharlal Nehru institute of advanced studies, Hyderabad, Telangana-500034, India

<sup>2</sup>Jawaharlal Nehru Technological University Ananthapur, Ananthapuramu-515002, Andhra Pradesh, India.

\*Corresponding author: gandhigia2017@gmail.com

Received 29 May 2018, Received in final form 26 July 2018, Accepted 26 July 2018

## Abstract

In this study, the adsorption potential of *Macrotyloma uniflorum* seed powder as bio active material for removal of Cr (VI) ions from wastewater has been investigated. The study involves batch type experiments to investigate the effect of initial concentration, adsorbent dose, contact time, temperature and pH of solution on adsorption process and the optimum conditions were evaluated. The adsorption process has fit pseudo first order kinetic models. Langmuir and Freundlich and Temkin adsorption isotherm models were applied to analyze adsorption data and both Freundlich and Temkin were found to be applicable to this adsorption process. Thermodynamic parameters, e.g.,  $G^\circ$ ,  $S^\circ$  and  $H^\circ$  of the on-going adsorption process have also been calculated and the sorption process was found to be endothermic. Finally, it can be seen that *Macrotyloma uniflorum* seed powder was found to be effective bio active material for the removal of Cr (VI) from aqueous solution.

**Keywords:** Adsorption, Kinetics, *Macrotylomauniflorum* seed powder, Bioactive material

## 1. Introduction

The natural resource is being contaminated every day by various anthropogenic activities such as rapid growth of population, urbanization and industrialization that ultimately make the environment polluted. Since recent years, sewage waters have been used for irrigation purposes [1]. There are greater concerns about heavy metal contamination [2, 3] in the receiving water system and land. The occurrence of toxic heavy metals in the soil is of geogenic or anthropogenic origin. Heavy metals from the point of origin and other sources can be transported to distant environments [4, 5]. High levels of heavy metals can damage soil fertility and may affect productivity [6, 7]. Heavy metals in the environment may also change plant diversity and affect aquatic life.

Chromium in trace concentration is an essential element in the diet, as it regulates the glucose metabolism in the human body. Excess amounts of chromium uptake are very dangerous due to its carcinogenic effect. Chromium in soils

affects plant growth [8], it is non-essential for microorganisms and other life forms and when in excess amounts it exerts toxic effect on them after cellular uptake. Cr (VI) is more toxic than Cr (III). Leather and chromium plating industries are the major causes for environmental influx of chromium [9, 10]. The movement of chromium and its bioavailability poses a potential threat to the environment.

In this context, it is important to note that, large numbers of leather industries are engaged in chrome tanning processes in Ethiopia. There is a possibility of chromium contamination in soils and waters around industrial sites. Cleaning up of the chromium-contaminated sites is a challenging task because removal of Cr (VI) in aqueous solution is very difficult. Hence, proper treatment of tannery wastewater is essential before releasing into the recipient environment. There are a number of methods employed [11-5] for removal of hexavalent chromium from industrial wastewater such as the use of various types of adsorbents.

## 2. Materials & Methods.

### 2.1.1. Selection of Adsorbent

*Macrotyloma uniflorum* is commonly known as Horse gram, belongs to the family Fabaceae polyphenols present in seed extract of *Macrotyloma uniflorum* were water soluble, heat stable, polar, non-tannin and non-protein in nature, which may favors the adsorption process. Taking all these factors into consideration *Macrotyloma uniflorum* seed powder is selected as an adsorbent.

### 2.1.2. Selection of optimum contact time

The contact time strongly influences the adsorption process, for this study an 1000 ml of different concentrations of chromium solutions were taken separately and they were mixed with optimum adsorbent dosage and stirred for different period of contact time i.e. for 1hr and time interval varies as 3,5,10,15.....60 min. After completion of 60 mints contact time the samples were filtered through watt man NO.1 filter paper and analyzed for chromium concentration using spectrophotometer method [16].

### 2.1.2. Determination of Optimum Dosage of Adsorbent

The effect of adsorbent dose on the removal of chromium, is studied in neutral condition (pH 7), at ambient temperature ( $25 \pm 2^\circ\text{C}$ ) and contact time of 60 minutes for initial chromium concentration of 4 mg/L. The added amount of adsorbent was varied from 0.2 g-1.2 g. After completion of optimum contact time period the solutions were filtered and analyzed for residual and removal of chromium concentrations respectively. The dosage which gives minimum residual concentration is chosen as optimum dosage [17].

### 2.1.3 Effect of Initial Concentration of ion

The adsorption of chromium onto various selected adsorbents was studied by varying initial chromium concentration using optimum adsorbent dosage, at ambient temperature ( $25 \pm 2^\circ\text{C}$ ) and contact time of 60 minutes. The filtered solutions were analyzed for residual and removal of chromium concentrations respectively [18].

### 2.1.4. Determination of Optimum pH

A series of conical flasks were taken with 1000 ml of 4 mg/L of chromium solution to determine the optimum pH by adding optimum adsorbent dosage at different pH. The pH of the flasks was adjusted ranging from 3.0 to 10.0. The flasks were kept at room temperature for optimum contact time. After stirring the samples are filtered and analyzed for the chromium and chromium concentration. The flask which gives minimum and

less concentrations (F) is selected as the optimum pH [19].

### 2.1.5. Effect of Temperature

Temperature has an important effect on the process of adsorption. The percentage of chromium adsorption is studied as a function of temperature. The batch experiments were performed at temperatures of  $0^\circ\text{C}$ ,  $30^\circ\text{C}$ ,  $40^\circ\text{C}$ ,  $50^\circ\text{C}$ , at different initial (1, 2, 3 and 4 mg/L) concentrations of chromium.

### 2.1.6. Adsorption Isotherm Models

The parameters obtained from the different models gives important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption isotherm models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid phase concentration were tested with the Langmuir, Freundlich and Tempkin isotherm equations [20]. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients.

#### 2.1.6(a). Temkin Adsorption Isotherm Model

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface [21-23]. The assumptions made by Temkin are

- ✓ Heat of adsorption decreases with surface coverage due to the interactions between adsorbent and adsorbate [24].
- ✓ Bonding energies are uniformly distributed up to certain binding energies. Depending upon these two factors Temkin proposed an empirical equation which is represented as follows [25 - 26]

$$q_e = B_T \ln K_T C_e \quad (1)$$

The linear form of temkin equation is as follows (Temkin and Pyzhav)

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (2)$$

Where T is absolute temperature (K), R is universal gas constant (8.314 J/mol.k),  $K_T$  is equilibrium binding constant (L/Mg),  $b_T$  is Variation of adsorption energy (kJ/mol)  $B_T$  is Temkin constant (kJ/mol).The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates. If the adsorption process follows Temkin adsorption isotherm model the graph between  $C_e$  versus  $q_e$  has to show a linear relationship.

### 2.1.6(b). Langmuir Adsorption Isotherm Model

Langmuir adsorption isotherm explains quantitatively the formation of monolayer adsorbate on outer surface of the adsorbent, and after that no further adsorption takes place. The theoretical Langmuir isotherm is valid for adsorption of solute from a liquid solution as monolayer adsorption on a surface containing a large number of identical sites. Langmuir isotherm model [27] explains uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. The Langmuir isotherm has an assumption that the adsorption occurs within adsorbent at specific homogeneous site. The linear form of Langmuir equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \quad (3)$$

Where  $q_e$  is adsorption capacity equilibrium,  $q_m$  is the maximum adsorption capacity,  $C_e$  is the solution concentration at equilibrium  $k_L$  is Langmuir constant.

### 2.1.6(c). Freundlich Adsorption Isotherm Model

The Freundlich equation is basically empirical but is often useful as a mean for data description. The equation generally agrees with the Langmuir equation and experimental data over moderate ranges of concentration [28]. This is commonly used to describe the adsorption characteristics for the heterogeneous surface [29]. The data often fit the empirical equation proposed by Freundlich.

$$q_e = k_f C_e^{\frac{1}{n}} \quad (4)$$

The linear form of Freundlich equation is as follows [30]

$$\log q_e = \log k_f + \frac{1}{n} (\log C_e) \quad (5)$$

Where  $k_f$  is the Freundlich adsorption capacity and  $n$  is the adsorption intensity. A plot of  $\log q_e$  versus  $\log C_e$  gives a linear line with slope of  $1/n$  and intercept of  $\log k_f$ .

### 2.1.7. Adsorption Kinetic models

In order to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, several kinetic models are used to test experimental data. The mechanism of adsorption involves the chemical reaction of functional groups present on the surface of the adsorbent and adsorbate. In present study the experimental data were tested with pseudo first order, pseudo Second order, Elovich model and intra particle diffusion models [31].

### 2.1.7(a). Pseudo first order equation:

Pseudo-first-order kinetic model, the Lagergren rate equation, has been the most widely used rate equation for assigning the adsorption of an adsorbate from a liquid phase since 1898 [32]. A simple kinetic analysis of adsorption is the pseudo-first-order equation in the form [33-34].

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (6)$$

Where  $k_1$  is the rate constant of pseudo-first-order adsorption and  $q_e$  denotes the amount of adsorption at equilibrium. After definite integration by applying the initial conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$ , the linear equation is as follows

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} X t \quad (7)$$

The plot of  $\log(q_e - q_t)$  versus  $t$  should give a straight line with slope of  $-k/2.303$  and intercept  $\log q_e$ . Pseudo first-order kinetic equation differs from a true first-order equation in following ways

- ✓ The parameter,  $k$  ( $q_e \cdot q_t$ ) does not represent the number of available sites,
- ✓ The parameter,  $\log(q_e)$  is an adjustable parameter and often it is found that it is not equal to the intercept of the plot of  $\log(q_e - q_t)$  versus  $t$ , whereas in a true first order model the value of  $\log q_e$  should be equal to the intercept.

Hence, pseudo first order kinetic model is used for estimating  $k$  alone, which is considered as mass transfer coefficient in the design calculations [35].

### 2.1.7(b). Pseudo second-order kinetics

As pseudo first-order kinetic model gives only  $k$  and as  $q_e$  cannot be estimated using this model, applicability of the pseudo second-order kinetics has to be tested for the estimation of  $q_e$  with the rate equation given by Ho 1995, [36]. The pseudo second order kinetic order equation expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

Where  $k_2$  is the rate constant of pseudo second order adsorption ( $g/mg/min$ ) and  $q_e$  is the equilibrium adsorption capacity ( $mg/gm$ ) [37]. The plot of  $t/q_t$  versus  $t$  should give a linear relationship which allows the computation of a second-order rate constant,  $k_2$  and  $q_e$ . The pseudo-second order model is based on the assumption that the rate limiting step may be chemical adsorption involving valence forces through sharing or exchange of electrons between the adsorbent and adsorbate [38].

### 2.1.7(c). Elovich Model

Elovich equation is also used successfully to describe second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate-adsorbent [39-40]. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation [41]. The Elovich or Roginsky-Zeldovich equation is generally expressed as follows [42 - 44, 23]

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (9)$$

Where,  $\alpha$  is the initial adsorption rate (mg/g/min),  $\beta$  is the desorption constant (g/mg). If the adsorption fits to the Elovich model, a plot of  $q_t$  versus  $\ln(t)$  should give a linear relationship with a slope of  $(1/\beta)$  and an intercept of  $1/\beta \ln(\alpha\beta)$ .

### 2.1.7(d). Intraparticle Diffusion Model

In adsorption studies it is mandatory to find out the rate limiting step. Therefore the results obtained from the batch adsorption experiments were used to study the rate limiting step. The rate limiting step might be film or intraparticle diffusion which was tested by plotting a graph between amount of ion adsorbed and square root of time [45].

$$q_t = K_{id} t^{1/2} + I \quad (10)$$

Where  $q_t$  is the amount of chromium and chromium adsorbed (mg/g) at time  $t$  (min), and  $I$  is the intercept (mg/g).  $k_{id}$  and  $I$  values are obtained from the slopes and intercept of the linear plot. If the postulated mechanism is correct, then a linear plot passing through the origin is obtained. Additionally, the value of the rate constant for diffusion is obtained from the slope of the line. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process. In general, a mass transfer process is diffusion controlled and its rate is dependent upon the rate at which components diffuse towards one another. The intraparticle diffusion model has been applied in three different forms:

(i) The amount of adsorption at any time,  $q_t$  is plotted against  $t^{1/2}$  to get a straight line passing through origin. This means that  $A$  is equal to zero which implies that the rate is not limited by mass transfer across the boundary layer. This occurs when a system is agitated and mixed to a sufficient extent (high turbulence);

(ii) Multi-linearity in  $q_t$  versus  $t^{1/2}$  plot is considered (that is, two or three steps are involved).

In this form, the external surface adsorption or instantaneous adsorption occurs in the first step; the second step is the gradual adsorption step, where intra-particle diffusion is controlling; and the third step is the final equilibrium step, where the solute moves slowly from larger pores to micro pores causing a slow adsorption rate. The time required for the second step usually depends on the variations of the system parameters such as solute concentration, temperature, and adsorbent particle size;

(iii)  $q_t$  is plotted against  $t^{1/2}$  to obtain a straight line but does not necessarily pass through the origin; that is, there is an intercept [46]. This implies that the rate is limited by mass transfer across the boundary layer. This occurs in a slowly stirred batch adsorption process.

### 2.1.8. Thermodynamic parameters

Thermodynamic parameters were calculated from the variation of the equilibrium constant,  $K_c$ , at different temperature by using following equation.

$$K_c = \frac{q_e}{C_e} \quad (11)$$

$K_c$  (L/g) values were obtained using the Khan and Sing method [47] by plotting  $\ln(q_e/C_e)$  versus  $q_e$  and extrapolating to zero. The intercept of the straight line with the vertical axis gives the values of  $K_c$ . The Gibbs free energy change of the adsorption process is related to  $K_c$  as in equation given below [48].

$$\Delta G^\circ = -RT \ln K_c \quad (12)$$

The changes in enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) for chromium and chromium adsorption were calculated from the slope and intercept of the plot of  $\ln K_c$  against  $1/T$  according to the van't Hoff equation [49].

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

Where  $\Delta S^\circ$  is change in entropy,  $\Delta H^\circ$  is change in enthalpy  $\Delta G^\circ$  is change in free energy. Plotting  $\ln K_c$  versus  $1/T$  shows straight lines. From their slope and intercept,  $\Delta H^\circ$  and  $\Delta S^\circ$  are determined. The negative values of  $\Delta G^\circ$  indicate a favourable and spontaneous process [42, 50].

### 2.1.9. Equilibrium parameter

In order to find out the efficiency of adsorption process, the dimensionless equilibrium parameter,  $R_L$  is calculated by using following equation [20, 51].

$$R_L = \frac{1}{1 + bC_o} \quad (14)$$

Where  $C_o$  = Initial concentration (mg/L),  $b$  is Langmuir isotherm constant. Values of the dimensionless equilibrium parameter explain the differences in the shapes of the isotherm. The  $R_L$  values lies between 0 and 1 indicate favourable adsorption. The  $R_L$  value above 1 indicates unfavourable.

### 2.1.10. Non-linear regression analysis

In this experimental study, a non-linear regression analysis was conducted to determine the isotherm and kinetic constants and statistical comparison values such as determination coefficient ( $R^2$ ), standard error of the estimate (SEE) and Absolute sum of squares (ASS). The batch adsorption data was evaluated using Graphpad prism scientific software. As regression models were solved, they were automatically sorted according to the goodness-of-fit system into a graphical interface. To determine the statistical significance of the predicted results 95 % confidence was used in the non-linear regression analysis.

## 3. Results & discussions

### 3.1. Effect of Contact time between Chromium and *Macrotyloma uniflorum* seed powder

The removal percentage is gradually increased with increases contact time, and reached equilibrium in 45 minutes (Fig.1). The time variation curve is smooth and continuous and this indicates the formation of monolayer coverage on the outer interface of the adsorbents [52]

### 3.2. Effect of Initial Chromium Concentration on *Macrotyloma uniflorum* seed powder

Optimum concentrations were determined after batch experimental studies done under various Chromium concentrations ranging between 50 to 200 mg/L. The adsorption efficiency increased with increase in metal ion concentration. The results obtained from the experimental studies are shown in Fig.2.

### 3.3. Effect of Adsorbent Dosages

The results of the adsorption equilibrium experiments using different amounts of adsorbent i.e. 0.2 -2.0 gm/L and results represented in Fig.3. It shows that the behaviour of *Macrotyloma uniflorum* seed powder with increasing the dosage. It was found that there is a sharp increase in the adsorption capacity with adsorbent dosage. It is evident that the percentage removal of Chromium increasing with increase in the dosage of adsorbent

due to the increased availability of the active sites and surface area for the adsorption of chromium.

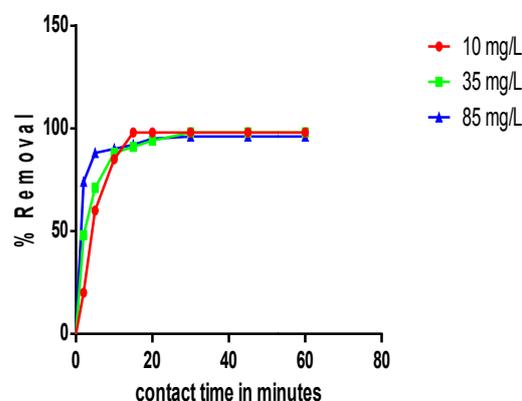


Fig. 1. Variation of contact time between Chromium and *Macrotyloma uniflorum* seed powder

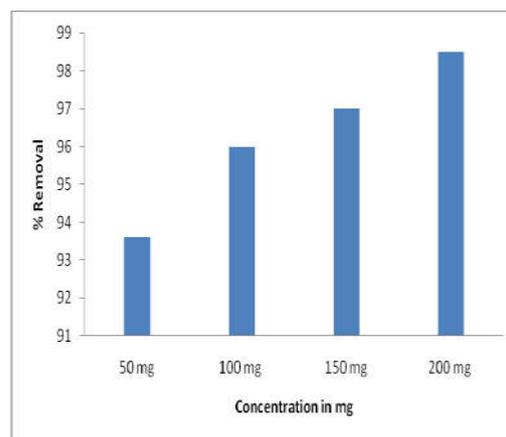


Fig. 2. Variation of initial concentration of Chromium on *Macrotyloma uniflorum* seed powder

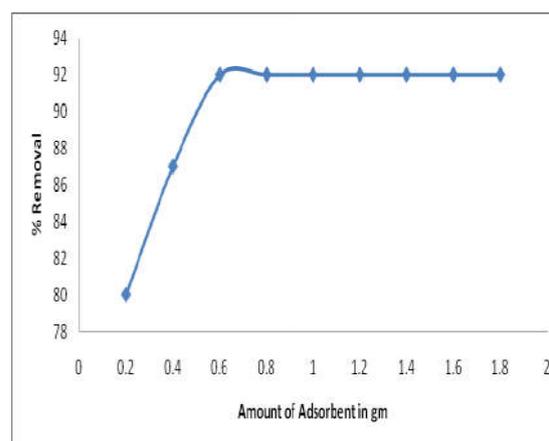


Fig. 3. Variation of *Macrotyloma uniflorum* seed powder dosages

**Table.1.** Isotherm kinetics for adsorption of Chromium (VI) by *Macrotyloma uniflorum* seed powder

S. No	Parameters	Temperature °C					
		0	30	40	50	60	80
<b>Temkin Adsorption Isotherm</b>							
01	R <sup>2</sup>	0.999	0.999	0.999	0.998	0.995	0.999
	ASS	0.632	0.834	1.659	7.578	19.90	0.699
	a <sub>r</sub>	-0.419	-0.608	-0.716	-1.133	-1.668	-0.563
	b <sub>r</sub>	0.965	0.964	0.968	0.967	0.962	0.977
<b>Langmuir Adsorption Isotherm</b>							
02	R <sup>2</sup>	0.571	0.835	0.964	0.778	0.972	0.403
	ASS	0.004	0.000	0.000	0.001	0.012	0.015
	Q <sub>0</sub>	1.139	1.137	1.136	1.168	1.206	1.216
	b <sub>L</sub>	-0.0013	-0.0012	-0.0012	-0.0014	-0.0016	-0.001
<b>Freundlich Adsorption Isotherm</b>							
03	R <sup>2</sup>	0.999	0.999	0.999	0.995	0.999	0.999
	ASS	0.000	0.009	0.007	0.002	0.000	0.000
	Log k <sub>r</sub>	-0.114	-0.105	-0.099	-0.125	-0.120	-0.120
	1/n	1.054	1.047	1.043	1.045	1.059	1.059

**Table. 2.** Kinetic parameters for adsorption of Chromium by *Macrotyloma uniflorum* seed powder

S. No	Parameters	Chromium concentration (10 mg/L)	Chromium concentration (35 mg/L)	Chromium concentration (85 mg/L)
<b>Pseudo first order kinetic model</b>				
01	R <sup>2</sup>	0.998	0.959	0.892
	ASS	0.000	0.032	0.036
	K <sub>1</sub>	0.096	0.059	0.055
<b>Pseudo Second order kinetic model</b>				
02	R <sup>2</sup>	0.986	0.877	0.786
	ASS	0.345	0.000	0.056
	K <sub>2</sub>	2.415 x 10 <sup>-3</sup>	1.742 x 10 <sup>-3</sup>	2.482 x 10 <sup>-3</sup>
<b>Elovich model</b>				
03	R <sup>2</sup>	0.806	0.877	0.786
	ASS	10.88	32.62	65.68
	α	0.949	1.183	2.527
	β	0.448	0.197	0.194
<b>Intraparticle diffusion model</b>				
04	R <sup>2</sup>	0.394	0.489	0.380
	ASS	33.99	135.9	190.5
	k <sub>id</sub>	0.174	0.423	0.401
	I	6.146	25.21	73.56

**Table.3.** Thermodynamic parameters of Chromium adsorption by *Macrotyloma uniflorum* seed powder

S. No	Temperature	ΔG° (KJ/ mol)	ΔS° ( KJ/ mol)	ΔH° (KJ/ mol)
01	273	-1296.6	4.711	-12.12
02	303	-1439.1		
03	313	-1486.6		
04	323	-1534.1		
05	333	-1581.6		
06	353	-1676.6		

**Table.4.** Equilibrium parameter RL values at different concentration and different temperatures

S.No	Temperature (°C)	Concentration of Chromium (mg/L) and RL values		
		10 mg/L	35 mg/L	85 mg/L
01	0	0.131	0.479	0.124
02	30	0.121	0.438	0.113
03	40	0.121	0.438	0.113
04	50	0.141	0.510	0.135
05	60	0.162	0.593	0.157
06	80	0.193	0.712	0.192

### 3.4. Effect of pH:

The effect of pH for the removal of Cr (VI) was shown in Fig.4. The role of hydrogen ion concentration was observed at different pH range of 2-9. The pH affects the solubility of chromium ion to a great extent. The pH of the aqueous solution is the controlling factor in the adsorption process; hence it become necessary to determine at what pH aloe, maximum adsorption will takes place. The maximum removal efficiency was 95% at neutral pH value (pH 7).

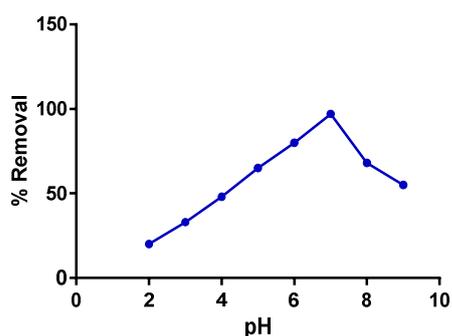


Fig. 4: Effect of pH on adsorption of chromium by *Macrotyloma uniflorum* seed powder

### 3.5. Effect of Temperature:

The adsorption of Cr (VI) by *Macrotyloma uniflorum* seed powder as a function of temperature is illustrated in Fig.5. The results showed that the adsorption capacity for Cr (VI) decreased from with increase temperature, indicating that the process is exothermic at low and medium concentrations, Hassan Zavvar Mousavi et al., 2012 [53] also reported same description in their studies. The adsorption capacity is increased with increase in temperature at higher concentrations.

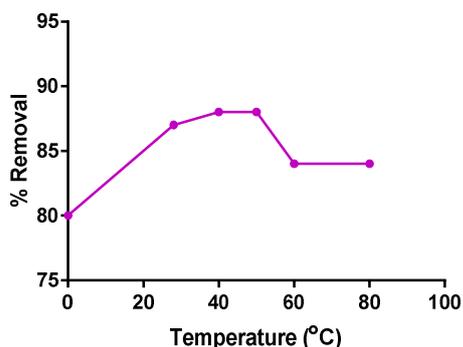


Fig. 5. Effect of temperature on adsorption process.

### 3.6. Adsorption Isotherm Data Analysis:

The experimental data tested with Temkin, Langmuir and Freundlich adsorption isotherm

studies and determined constant values and other parameters.

#### 3.6(a). Temkin Adsorption Isotherm:

Fig.6 (a) & (b) showing relation between  $C_e$  and  $q_e$ , from the figures and Table. 1 it was observed that the adsorption of Chromium by *Macrotyloma uniflorum* seed powder is following Temkin adsorption isotherms. The straight line of the graph indicates that adsorption is practically proportional to concentration. The adsorption capacity increases, with increase in temperature. Adsorption (both physical and chemical) processes are exothermic in nature.

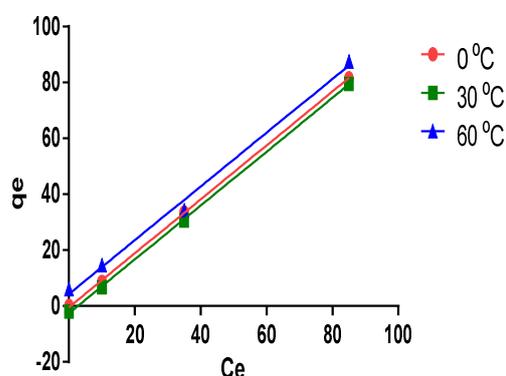


Fig. 6(a). Temkin adsorption isotherm at different temperatures

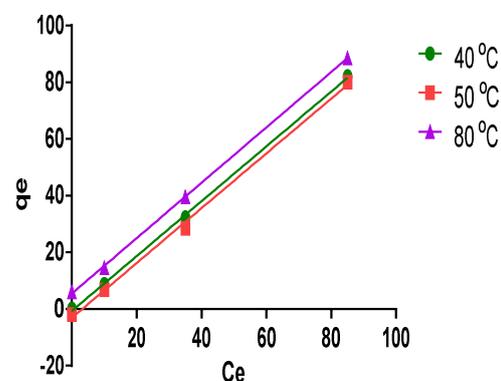


Fig. 6(b). Temkin adsorption isotherm at different temperatures.

#### 3.6(b). Freundlich Adsorption Isotherm:

Freundlich isotherm constants of the adsorbent were calculated from the slope and intercept of the linear plot  $\log q_e$  vs  $\log C_e$ . The values of  $1/n$  lying between 0 and 1 confirm the favourable conditions for adsorption [54]. Linear plots of  $\log C_e$  vs  $\log q_e$  at different temperatures are applied to confirm the applicability of Freundlich models as shown in Fig.7.

The calculated values of Freundlich isotherms model are listed in Table. 1.

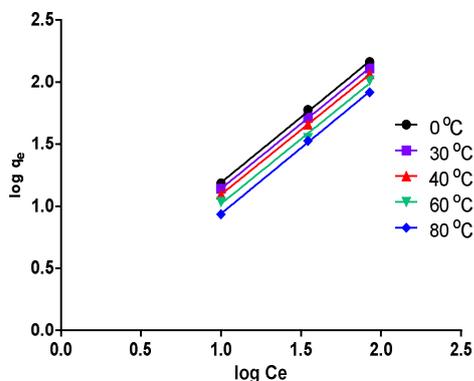


Fig. 7. Freundlich adsorption isotherm for removal of chromium by *Macrotyloma uniflorum* seed powder

**3.6(c). Langmuir Adsorption Isotherm:**

The adsorption process of Chromium (VI), with *Macrotyloma uniflorum* seed powder at different temperature has shown in Fig.8. The constant values for Langmuir isotherms were given in Table. 1. From the Fig.8 and Table. 1, it was evident that the correlation coefficient values of Langmuir isotherm is less compare to Freundlich adsorption isotherms. It indicates that adsorptive removal of chromium process more favourable to Freundlich isotherm compare to Langmuir isotherm.

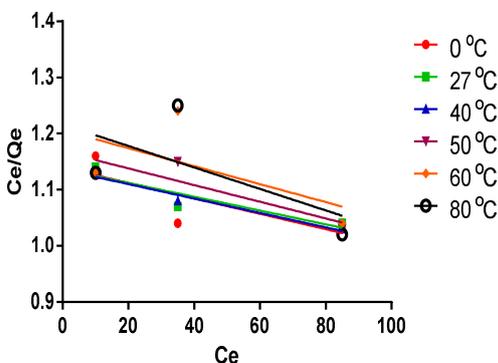


Fig. 8. Langmuir Adsorption isotherm for removal of chromium by *Macrotyloma uniflorum* seed powder

**3.7. Adsorption Kinetic Models**

**3.7(a). Pseudo first order kinetic model:**

The plot of  $\log (q_e - qt)$  versus  $t$  should give a straight line (Fig.9) from which rate constant  $k_1$  and  $q_e$  can be calculated from the slope and intercept of the plot, respectively. If the plot was found to be linear with good correlation coefficient, it indicates that Lagergren's equation is appropriate to Chromium sorption on *Macrotyloma uniflorum* seed powder. The constant values and calculated values

are given in Table. 2. Form Fig.9 and Table. 2, it was concluded that the adsorption of chromium by *Macrotyloma uniflorum* seed powder is not fits into Lagergren kinetic model.

**3.7(b). Pseudo Second order kinetic model**

Pseudo second order kinetic plot of  $(t/qt)$  versus  $(t)$  gave the perfect straight line for the adsorption of chromium by *Macrotyloma uniflorum* seed powder. The Fig.10, showing the linear relation of pseudo second order kinetic model for the removal of chromium. From the graph it was concluded that the adsorption reaction also can be approximated with pseudo-second order kinetic model.

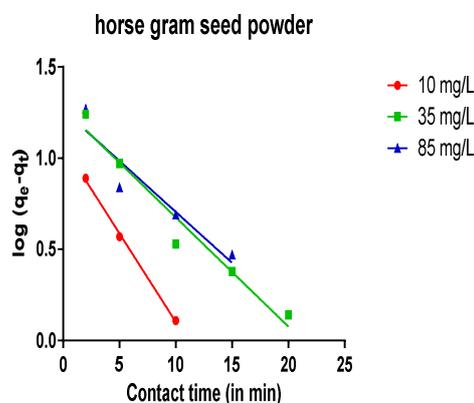


Fig. 9. Pseudo first order kinetic model for adsorption of Chromium (VI)

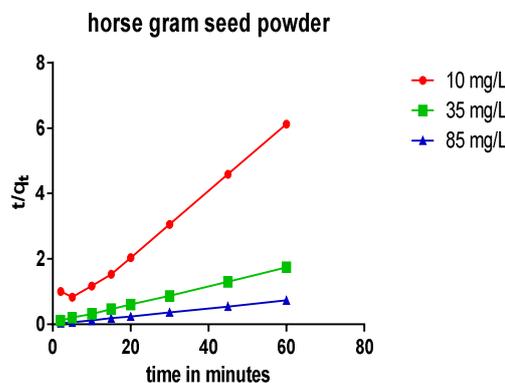


Fig. 10. Pseudo Second order kinetic model on adsorption of chromium

**3.7(c). Elovich model**

If the adsorption of aqueous Chromium solution by *Macrotyloma uniflorum* seed powder fits to the Elovich model, a plot of  $q_t$  versus  $\ln (t)$  should give a linear relationship with a slope of  $(1/\beta)$  and an intercept of  $1/\beta \ln (\alpha\beta)$ . The results of Elovich plot for the adsorption of Chromium solution by *Macrotyloma uniflorum* seed powder at various

initial concentrations are given in Fig.11. From the slope and intercept of Fig.11, the constant values were calculated and listed in Table. 2. The calculated values ( $\alpha, \beta$ ) obtained from graph compared with experimental values and they were very lower than experimental values. The  $R^2$  values are very poor, which indicating that adsorption of chromium by *Macrotyloma uniflorum* seed powder does not describe Elovich model. Elovich model mainly applicable for chemical adsorption kinetics more.

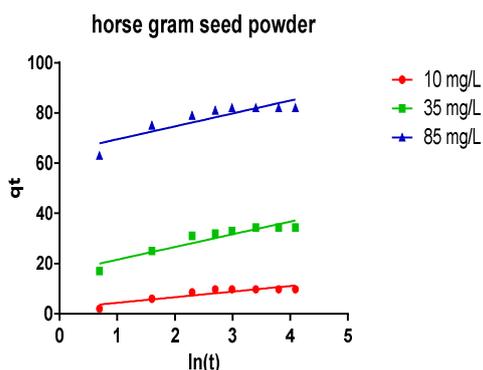


Fig. 11. Elovich model plots for adsorption of chromium *Macrotyloma uniflorum* seed powder.

**3.7(d). Intraparticle diffusion model:**

According to this model, the plot of uptake  $q_t$  versus the square root of time ( $t^{1/2}$ ) should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step.

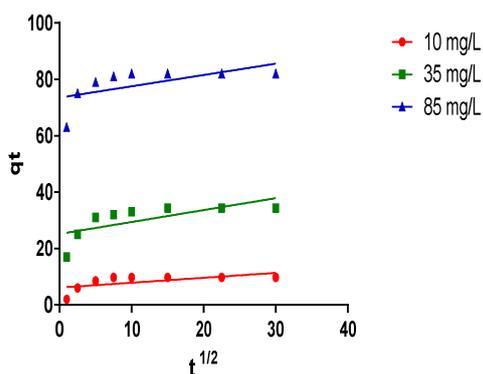


Fig. 12. Intraparticle Diffusion plots for adsorption of chromium *Macrotyloma uniflorum* seed powder.

When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further show that the intraparticle diffusion is not only rate limiting step, but also other kinetic models may control the rate of adsorption, all which may be operating

simultaneously. The intraparticle diffusion  $K_1$  values were obtained from the slope of the straight line portions of plot (Fig.12). The correlation coefficient values ( $R^2$ ) for intraparticle diffusion model are between 0.380 to 0.489, at room temperature, which listed in Table. 2. It was observed that intraparticle rate constant values were decreased with initial chromium concentration.

**4. Thermodynamic Parameters:**

From the Fig.13  $K_c$  values were found. The thermodynamic constants, Gibb's free energy ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ) are calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process.

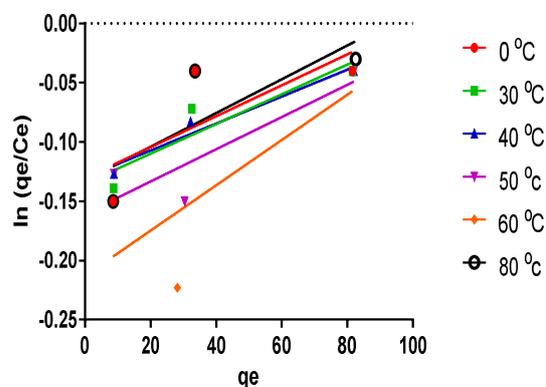


Fig. 13. Relationship between  $\ln(qe/Ce)$  and  $q_e$  for the removal of chromium by *Macrotyloma uniflorum* seed powder.

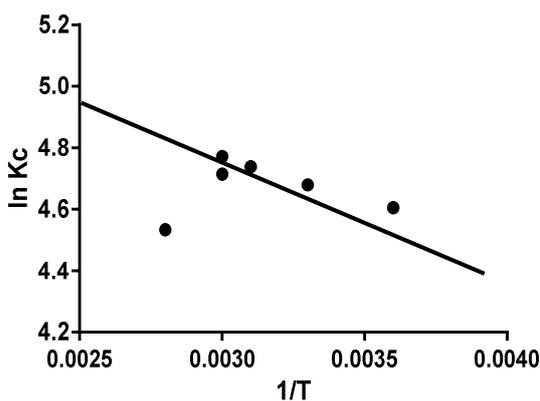


Fig. 14. Relationship between  $\ln kc$  and  $1/T$  for the removal of chromium by *Macrotyloma uniflorum* seed powder

The enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ) were calculated from slope and intercept of the graph of the  $\ln kc$  versus  $1/T$  values (Fig.14). The calculated values are tabulated in Table. 3. The negative values of  $\Delta G^0$  indicating that

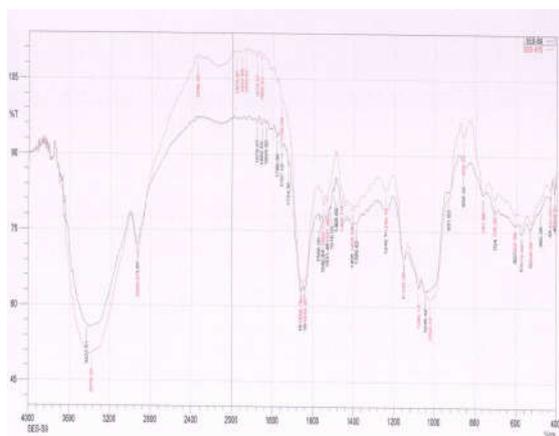
the feasibility of sorption process and the spontaneous nature of adsorption. The positive value of  $\Delta H^0$  obtained indicated the endothermic nature of the process. The positive  $\Delta S^0$  values indicated the affinity of the adsorbent for Cr (VI).

### 5. Equilibrium parameter:

Values of the dimensionless equilibrium parameter,  $R_L$ , of different temperatures are calculated for the initial concentrations of Chromium (VI) and are given in Table. 4. The parameters explain the differences in the shapes of the isotherm. The observed  $R_L$  values for Chromium (VI) are between 0 to 1 and it indicative of the favourable adsorption.

### 6. Fourier Transform Infrared Spectroscopy

The FTIR spectrum of *Macrotyloma uniflorum* seed powder before and after adsorption is represented in Fig.15. -OH peak is represented by  $3427.51\text{ cm}^{-1}$  and after adsorption it is shifted to  $3379.51\text{ cm}^{-1}$  indicating the involvement of -OH group present in carbohydrates, fatty acids, proteins, units of lignin, cellulose and absorbed water. The band at  $2929.87\text{ cm}^{-1}$ , before and after adsorption represents the presence of alkane group.



**Fig. 15.** FTIR spectrum of *Macrotyloma uniflorum* seed powder before and after adsorption of chromium.

A prominent peak at  $2349.30\text{ cm}^{-1}$  is observed in spectrum of *Macrotyloma uniflorum* seed powder after adsorption. This result indicating that alkane group is involving in binding with chromium molecules present in aqueous solution. From the FTIR spectrum of chromium loaded *Macrotyloma uniflorum* seed powder, it was observed there is a shift in the wave number of dominant peaks associated with loaded metal. This shift indicates the binding of chromium (VI) ions, to the surface of *Macrotyloma uniflorum* seed powder. The maximum shift of peaks is observed in the region of 1800-

$2000\text{ cm}^{-1}$ , which indicating that the involvement of lignin and cellulose in binding the ions of chromium.

### 7. Conclusions:

In this study, removal of Chromium (VI) is investigated using *Macrotyloma uniflorum* seed powder at optimal removal conditions by using batch adsorption experiments. From the experimental results it was concluded that the adsorption process of removal of Chromium (VI) by *Macrotyloma uniflorum* seed powder is completed in relatively short time periods. Maximum removal efficiencies were succeeded within 45 minutes at higher concentration. The statistical and constant values are evaluated according to the Langmuir, Freundlich and Temkin adsorption isotherms which are generally used to describe the adsorption processes. It is studied that Temkin and Freundlich adsorption isotherm models are fits very well. Chromium (VI), adsorption from aqueous solutions using *Macrotyloma uniflorum* seed powder is well described with both pseudo first order and pseudo second order kinetic models. As a result of this study it may be concluded that *Macrotyloma uniflorum* seed powder may be used for removal of toxic chemicals and heavy metals along with chromium (VI) pollutants from waste water since it is a low cost abundant and locally available adsorbent.

### Reference:

- [1]. L. Vasseur, C. Cloutier, C. Anseau, "Effects of repeated sewage sludge application on plant community diversity and structure under agricultural field conditions on Podzolic soils in eastern Quebec", *Agri. Ecosys. Environ.* 81 (2000) 209.
- [2]. D. T. Gardiner, R. W. Miller, B. Badamchian, A. S. Azzari, D. R. Sisson, "Effects of repeated sewage sludge applications on plant accumulation of heavy metals", *Agri. Ecosys. Environ.* 55 (1995) 1.
- [3]. T. J. Logan, R. L. Chaney, "Proceedings of the workshop on utilization of municipal wastewater and sludge on land", University of California, Riverside. 235-326 (1983).
- [4]. A. Andersen, M. F. Hovmand, I. Johnson, 1978. Heavy metal deposition in the Copenhagen area", *Environmental Pollut.* 17 (1978) 133.
- [5]. E. Steinnes, "Atmospheric deposition of heavy metals in Norway studied by analysis of moss samples using neutron activation analysis and atomic absorption spectrometry", *J. Radioanal. Chem.* 58 (1983) 387.
- [6]. A. C. Chang, T. C. Granato, A. L. Page, "A methodology for establishing phytotoxicity criteria for chromium, copper, nickel and zinc

- in agriculture land application of municipal sewage sludges”, *J. Environ Qual.* 27 (1992) 521.
- [7]. P. S. Hooda, B. J. Alloway, “The plant availability and DTPA extractability of trace metals in sludge-amended soils”, *Sci. Total Environ.* 149 (1994) 39.
- [8]. A. Shanker, M. Djanaguiraman, G. Pathmanabhan, Proceedings of the international conference on water and environment, India. 9-13 (2003).
- [9]. A. J. M. Baker, S. P. McGrath, C. M. D. Sidoli, R. D. Reeves, “Possibility of in situ heavy metal decontamination of polluted soils using crops of metal accumulating plants”, *Res. Cons. Recy.* 11 (1994) 41.
- [10]. I. Barnhart, “Occurrences, uses & properties of Chromium”, *Reg. Toxicol. Pharma.* 26 (1997) 53.
- [11]. V. M. Boddu, K. Krishnaiah, L. T. Jonathan, E. D. Smith, “Removal of hexavalent chromium from wastewater using a new composite chitosan biosorbent” *Environ. Sci. Technol.* 37 (2003) 4449.
- [12]. L. Dupont, E. Guillon, “Removal of Hexavalent Chromium with a Lignocellulosic Substrate Extracted from Wheat Bran”, *Environ. Sci. Technol.* 37 (2003) 4235.
- [13]. M. Dinesh, P. S. Kunwar, K. S. Vinod, “Removal of hexavalent chromium from aqueous solution using low cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth”, *Ind. Eng. Chem. Res.* 44 (2005) 1027.
- [14]. V. K. Gupta, M. Gupta, S. Sharma, “Process development for the removal of lead and chromium from aqueous solutions using red mud-an aluminium industry waste”, *Wat. Res.* 35 (2001) 1125.
- [15]. G. Saumyen, B. Puja, “Title of paper missing”, *Wat. Environ. Fed.* 77 (2005) 411.
- [16]. D. Sirisha, Smita Asthana, N. Gandhi, M. Hasheena, “Adsorptive removal of aqueous SO<sub>2</sub> by using Orange Peel Powder”, *Indian J. Scie.*, 12 (2015) 39.
- [17]. N. Gandhi, D. Sirisha, Smita Asthana, “Bio adsorption of Alizarin red dye using immobilized *Saccharomyces cerevisiae*”, *Int. Res. J. Nat & Appl. Sci.* 2 (2015) 1.
- [18]. D. Sirisha, K. Mukkanti, N. Gandhi, “Adsorptive Removal of SO<sub>2</sub> by using Magnesium Carbonate (MgCO<sub>3</sub>)”, *Int. J. green Herb. Chem.*, 2 (2013) 576.
- [19]. N. Gandhi, D. Sirisha, Smita Asthana, A. Manjusha, “Adsorption studies of fluoride on multani matti and red soil”, *Res. j. chem. sci.* 2 (2012) 1.
- [20]. M. I. Temkin, V. Pyzhev, “Kinetic of Ammonia Synthesis on Promoted Iron Catalyst”, *Acta Phy. Chem, URSS* 12 (1940) 327.
- [21]. Y. S. Ho, J. F. Porter, G. McKay, “Equilibrium Isotherm Studies for Sorption of Divalent Metal ions onto Peat, Copper, Nickel and Lead single Component Systems, Water”, *Air. Soil, Pollu.* 141 (2002) 1.
- [22]. Z. Chen, W. Ma, M. Han, “Biosorption of Nickel and Copper onto Treated Alga (*Undriapinnarlifida*). Application of Isotherm and Kinetic Models”, *J. Hazar. Mater.* 155 (2008) 327.
- [23]. P. Brow, I. Jetcoat, D. Parrisha, S. Gilla, E. Grahams, “Evaluation of the Adsorptive Capacity of Peanut hull Pellets for Heavy Metals in Solution”, *Advanc. Envir. Res.* 4 (2008) 19.
- [24]. E. S. Cossich, C. R. G. Tavares, T. M. K. Ravagnani, “Biosorption of Chromium (III) by *Sargassum Sp. Biomass*”, *Elctro. J. Biotech.* 5 (2002) 133.
- [25]. I. Langmuir, “The Adsorption of Gases on Plane Surfaces of Glass Mic and Platinum”, *J. American Chem. Soci.* 40 (1918) 1361.
- [26]. A. R. Tembhurkar, D. Shipa, “Studies on Fluoride Removal using Adsorption Process”, *J. Envir. Sci. Eng.* 48 (2006) 151.
- [27]. M. Dakiky, M. Khamis, A. Manassra, M. Mereb, “Selective Adsorption of Chromium (VI) in Industrial Wastewater using Low-Cost Abundantly Available Adsorbents”, *Advanc. Envir. Res.* 6 (2002) 533.
- [28]. H. M. F. Freundlich, “Over the Adsorption in Solution”, *J. Phy. Chem.* 57 (1906) 385.
- [29]. E. Demirbas, M. Kobya, E. Sentark, T. Ozkan, “Adsorption Kinetics for the Removal of Chromium (VI) from Aqueous Solution on the Activated Carbons Prepared from Agricultural Waste”, *Water SA* 30 (2004) 533.
- [30]. S. Lagergren, “About the Theory of so Called Adsorption of Soluble Substances, *Kungliga Svenska Vetenskapsakademiens Handlingar*, 24 (1898) 1.
- [31]. L. Deng, Y. Su, H. Su, X. Wang, X. Zhu, “Sorption and Desorption of Lead (II) from Wastewater by Green Algae (*Cladophora fascicularis*)”, *J. Hazar. Mater.* 143 (2007) 220.
- [32]. S. Doyurum, A. Celik, “Pb (II) and Cd (II) Removal from Aqueous Solution by Olive Cakes”, *J. Hazar. Mater. B.* 138 (2006) 22.
- [33]. G. Suresh, B. V. Babu, “Removal of Toxic Metal Cr (VI) from Aqueous Solutions using Saw Dust as Adsorbent. Equilibrium, Kinetics and

- Regeneration Studies". Chem. Eng. J. 150 (2009) 352.
- [34]. Y. S. Ho, "Adsorption of Heavy Metals from Waste Streams by Peat", Ph.D. Thesis, University of Birmingham, Birmingham UK (1995).
- [35]. H. Elifantz, E. Telor, "Heavy Metal Biosorption by Plant Biomass of the Macrophyte (*Ludwigia stolonifera*)", Water Air and Soil Pollution, 141 (2002) 207.
- [36]. Y. S. Ho, G. Mcay, "Study of the Sorption of Divalent Metal ions to Peat", Adsorption Sci. Technol. 18 (2008) 639.
- [37]. S. M. Yakout, E. Elsherif, "Batch Kinetics, Isotherm and Thermodynamic Studies of Adsorption of Strontium from Aqueous Solutions onto Low-Cost rice Straw Based Carbons", Carbon Sci. Technol. 1 (2010) 144.
- [38]. D. L. Sparks (1989) "Kinetics of Soil Chemical Process", Academic Press, New York, USA.
- [39]. J. Zhang, R. Stan forth, "Slow Adsorption Reaction between Arsenic Species and Geothite. Diffusion or Heterogeneous Surface Reaction Control", Langmuir 21 (2005) 2895.
- [40]. M. J. D. Low, "Kinetics of Chemisorption of Gases on Solids", Chem. Rev. 60 (1960) 267.
- [41]. S. H. Chien, W. R. Clayton, "Application of Elovich Equation to the Kinetics of Phosphate Release and Sorption on Soils", Soil Sci. Soci. American J. 44 (1980) 265.
- [42]. D. L. Sparks (1986) "Kinetics of Reaction in Pure and Mixed Systems in Soil Physical Chemistry", CRC Press, Boca Raton.
- [43]. W. J. Weber, J. C. Morris, "Kinetics of Adsorption on Carbon from Solution", J. Sanitary Eng. Div. American Soci. Chem. Eng. 89 (1963) 31.
- [44]. F. Wu, R. Tseng, R. Juang, "Initial behaviour of Intraparticle Diffusion Model used in the Description of Adsorption Kinetics", Chem. Eng. J. 153 (2009) 1.
- [45]. A. A. Khan, R. P. Singh, "Adsorption Thermodynamics of Carbofuran on Sn (IV) Arseno silicate in H<sup>+</sup>, Na<sup>+</sup> and Ca<sup>2+</sup> forms", Colloids. Surface. 24 (1987) 33.
- [46]. H. Uslu, I. Inci, "Adsorption Equilibria of L - (+) - Tartaric Acid onto Alumina". J. Chem. Eng. Data, 54 (2009) 1997.
- [47]. P. N. Palanisamy, P. Sivakumar, "Adsorption Studies of Basic red 29 by a Non-Conventional Activated Carbon Prepared from *Euphorbia Antiguorum* L. Inter. J. Chem. tech. Res. 1 (2009) 502.
- [48]. M. Karthikeyan, K. P. Elongo, "Removal of Fluoride from Aqueous Solution using Graphite. A Kinetic and thermodynamic Study", Indian J. Chem. Technol. 15 (2008) 525.
- [49]. N. Gandhi, D. Sirisha D, K. B. Chandra Shekar, "Bioremediation of Wastewater by using *Strychnos Potatorum* Seeds (Clearing nuts) as Bio Adsorbent and Natural Coagulant for Removal of Fluoride and Chromium", J. Inter. Acad. Res. Multidiscip. 3 (2014) 253.
- [50]. N. Gandhi, D. Sirisha, M. Hasheena, Smita Asthana, "Eco-friendly Method for Synthesis of Copper Nanoparticles and Application for removal of Aqueous Sulphur Dioxide (SO<sub>2</sub>) and Nitrogen Dioxide (NO<sub>2</sub>)", Int. J. Engg. Res. & Sci. & Tech. 3 (2014) 253.
- [51]. N. Gandhi, D. Sirisha, Smita Asthana, "Bio adsorption of Alizarin red dye using immobilized *Saccharomyces cerevisiae*. Int. Res. J. Nat. & Appl. Sci. 2 (2015) 1.
- [52]. N. D. Pragnesh, K. Satindar, K. Ekta, "Removal of eriochrome black-T by adsorption onto eucalyptus bark using green technology". Indian J. Chem. Technol. 18 (2011) 53.
- [53]. Z. H. Mousavi, A. Hosseinifar, V. Jahed, "Studies of adsorption thermodynamics and kinetics of Cr (III) and Ni (II) removal by polyacrylamide", J. Serb. Chem. Soc. 77 (2012) 393.
- [54]. G. Jayapriya, F. Gricilda Shoba, "Pupicidal Activity and Morphological Deformities of *Justicia Adhatoda* Leaf Extracts Against Filarial Vector, *Culex Quinquefasciatus* And Dengue Vector, *Aedes Aegypti*, World J. Pharm. Pharm. Sci., 4 (6), 757-765.